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In a previous paper[1] (hereafter referred to as I), fine structure (fs) and hyperfine structure (hfs) constants of the $2p$ and $3p$ $^3\Pi_u$ states of H_2 have been calculated. In a recent congress,[2] measurements by Freund and Miller upon the $4p$ $^3\Pi_u$ state have been reported. The programs described in I have therefore been used to calculate fs and hfs constants of the next two higher $4p$ and $5p$ $^3\Pi_u$ states. The results for the five interatomic distances for which Rothenberg and Davidson[3] have calculated wavefunctions are given in Table I.

In Table II, the equilibrium values ($v = -\frac{1}{2}$) and the variations per vibrational quantum are displayed for the various fs and hfs constants of the 3, 4, and $5p$ $^3\Pi_u$ states. The vibrational averaging, made with the method described in I caused us some trouble. Table II shows that taking into account the quadratic β term of Eqs. (12) and (13) of I gives results much worse than excluding it. This might be for the following reason. β is very small for most of the properties, causing typically a variation of 0.1% over the range of R used, whereas the linear term α causes a variation of 10% over the same range. This little curvature can be completely upsetted by a curvature due to some systematic defect of the wavefunction used, e.g., lack of exponent optimization at each value of R. Unfortunately for the vibrational variation the influence of β, for which the dependence is direct, is the same order of magnitude as the influence of α, for which the dependence is only upon its product with the little coefficient of anharmonicity k_1 of the potential curve.

For the accuracy of the equilibrium values, the influence of β is negligible. In Table II are compared our theoretical and the experimental (Born Oppenheimer "deperturbed") values of Freund and Miller.[4-6]

Very similar conclusions can be given for this $4p$ level as for the $2p$ and $3p$ ones, i.e., 1% for one electron coefficients, 2%–4% for two electrons coefficients except for A. The reason for this bad result is probably that the A coefficient is the difference between two larger coefficients $A1$ and $A2$. If it is supposed that the whole error comes from the two electrons $A2$ coefficient, it

TABLE I. fs and hfs constants as a function of internuclear distance.

R(a.u.)	B_0(MHz)	B_2(MHz)	A_2(MHz)	A_1(MHz)	a(MHz)	a_F(MHz)	c(MHz)	d(MHz)
				$4p\,^3\Pi_u$				
1.90	−165.44	−445.00	−1179.0	729.38	2.218	483.91	70.750	−1.3980
1.95	−160.89	−433.79	−1150.8	709.57	2.158	472.02	67.635	−1.3566
2.00	−156.28	−422.32	−1121.1	688.81	2.095	460.88	64.701	−1.3137
2.05	−151.31	−409.77	−1087.9	665.95	2.026	450.41	61.395	−1.2672
2.10	−145.78	−395.64	−1049.9	640.32	1.948	440.57	59.325	−1.2157
				$5p\,^3\Pi_u$				
1.90	27.61	−47.44	−107.70	73.21	0.223	485.28	71.68	−0.0902
1.95	26.91	−46.01	−104.50	71.15	0.216	473.38	68.54	−0.0876
2.00	26.34	−44.94	−102.12	69.62	0.212	462.23	65.58	−0.0857
2.05	25.89	−44.26	−100.62	68.60	0.209	451.74	62.79	−0.0845
2.10	25.03	−44.00	−100.08	68.18	0.207	441.87	60.15	−0.0842

TABLE II. fs and hfs constants. Comparison with experiment.

	$3p\,^3\Pi_u$					$4p\,^3\Pi_u$					$5p\,^3\Pi_u$	
Constant	Pe theor.[a]	Pe exptl.	$\Delta P/\Delta v$ theor.[b]	$\Delta P/\Delta v$ theor.[a]	$\Delta P/\Delta v$ exptl.	Pe theor.[a]	Pe exptl.	$\Delta P/\Delta v$ theor.[b]	$\Delta P/\Delta v$ theor.[a]	$\Delta P/\Delta v$ exptl.	Pe theor.[a]	$\Delta P/\Delta v$ theor.[a]
a_F	462	465	−4	−18	−10	458		−3	−17		463	−18
a	6.0	6.9	−0.13	−0.24	−0.3	2.1	2.5	−0.2	−0.1	−0.4	0.21	−0.006
c	64.3		−1.37	−4.7		64.0		−1	−4.5		65.9	−4.7
d	−3.7		0.08	0.14		−1.29		0.14	0.07		−0.08	0.002
$c-3d$	75.4	72	−1.61	−5.1	−2.7	67.9	67	−1.4	−4.7	−4.3	66.1	−4.7
B_0	−398	−377	12	18		−154	−160	15	8		−26.4	−1
B_2	−1116	−1089	28	41		−417	−433	40	19		−45.4	1.4
$-6^{1/2}B_2+B_0$	2336	2289	−56	−83	−96	867	900	−84	−39	−41	138	−4.5
$6^{1/2}B_2+B_0$	−3132	−3044	80	119	148	−1175	−1220	113	54	55	−85	2.5
A_1	1980		−41	−79		680		−76	−35		70	−2
A_2	−3033		74	114		−1107		120	51		−103	3
A	−1053	−842	32	35	55	−427	−314	44	16	15	−33	1

[a]Without β term.

[b]With β term.

can be concluded that $A2$ is 6% too great, which is consistent with the accuracy of B_0 and B_2. The accuracy of $A2$ is somewhat worse because $A2$ itself is the sum of four terms of various signs as shown in Eq. (2) of I.

The $5p\ ^3\Pi_u$ results have been included for the sake of completeness since we had R. D.[3] wavefunctions for this state. But these results are dubious: these wavefunctions include powers in ξ up to 3 only, whereas proper account of the quasihydrogenoid $5p$ electronic state would need a ξ^4 term.

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